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Remarks/Arguments

Attorney for Applicants submits this Amendment to distinguish the presently claimed invention from the references cited by the Examiner. It is believed that the presently claimed invention is patentably distinct from the reference's teachings and, therefore, in condition for allowance. Such action is respectfully solicited.

The Examiner has noted that the subject matter of Claims 42-43, 49, 51-52 and 66 are directed to allowable subject matter. Applicants have amended independent Claims 32 and 57 to incorporate the subject matter deemed allowable. Thus, it is respectfully submitted that said independent claims and the claims directly or indirectly dependent thereon are all directed to allowable subject matter and are in proper form to be found in condition for allowance.

To fully distinguish the claims, as presently amended, from the prior art, Applicant's have the following remarks:

The Examiner has rejected Claims 32-35, 44, 46-47, 57-59, 61-62 and 64-65 under 35 USC 102 (b) as being fully anticipated by the teachings of Kumar et al. (US Patent 5,079,202). It is respectfully submitted that the teachings of Kumar et al. does not teach nor make obvious the presently claimed invention and, therefore, this rejection is unwarranted and should be withdrawn.

Kumar et al. discloses catalyst compositions that are composed of (1) a zeolite, (2) an inorganic matrix, and (3) a polycite. The Examiner has noted

that the present claims contain "consisting essentially of" language and, thereby, limit the scope of the claims to the defined components and those that do not affect the basic and novel characteristics of the composition.

The presently claimed invention is directed to a composition containing a very high loading of specifically defined zeolites. The claims, as presently amended, require the composition to be composed of greater than 70 wt percent of specifically defined zeolite materials. Kumar et al. teachings can not be deemed to direct one to compositions having such high loading of zeolite nor to the use of the specifically defined zeolite material.

Although Kumar et al. contains a teaching to the use of a broad range of from 5 to 70 weight percent of zeolite, the reference, by its illustrative examples (See Table B) directs one to utilize lower amounts than the upper limit taught. Each example illustrating thier preferred embodiment, utilizes 35 weight percent zeolite. Such showing directs one skilled in the art away from the zeolite content of the presently claimed invention.

Further, Kumar et al. teaches that such composition should contain pollucite in from 1 to 50 weight percent of the composition. As previously discussed, Kumar et al. clearly teaches that pollucite has a material effect on the resultant composition. Specifically, the reference states that the activity characteristics of thier composition can "be improved by the addition of about 1 to 50 weight percent of pollucite."

The Examiner has suggested that the burden of showing that the addition of pollucite would materially effect the characteristics of the presently claimed composition rests on Applicants. Such is not so when the reference

teaching, per se, provides a teaching of the material effect attained by the additive.

Finally, it is known by those skilled in the art that catalyst systems based on zeolites are poisoned when contacted with a combination of an alkali metal and vanadium. The zeolite composition of Kumar et al., which contains pollucite, would have shortened life. The pollucite provides the alkali metal (Cs) and the petroleum stream, being treated by the catalyst composition, would provide the vanadium. The shortcoming is discussed in *Effect of Sodium Deposition of FCC Catalysts Deactivation* by Tangstad et al., *Applied Catalyst A: General* 150 (1997) 85-99; *Pathways for Y Zeolite Destruction: The Role of Sodium and Vanadium*, by Xu et al., *J. of Catalysis*, 207, 237-246 (2002); *Effect of Vanadium on USY zeolite destruction in the presence of sodium ions and steam* by Hagiwara et al., *Applied Catalysis A: General* 249 (2003) 213-228. Copies of these references are attached hereto as Appendix II of this paper.

Applicants have unexpectedly found that the defined components of the presently claimed invention can be formed to achieve a catalyst useful in FCC application, which exhibits high kinetic conversion activity of at least 3 and has low Davison Attrition Index of less than 20. The presently claimed composition does not by definition contain a component, such as pollucite, that would materially effect the catalyst composition (as taught by Kumar et al. to raise the conversion activity and, as known in the art, to promote poisoning of the catalyst during use).

It is respectfully submitted that the claims, as presently amended, are not taught nor made obvious by the teachings of Kumar et al. Withdrawal of the rejection based on this art is respectfully solicited.

Claims 32-39, 41, 44 and 46 are rejected under 35 USC 102(b) over the teachings of Kukes et al. It is respectfully submitted that the claims, as presently amended, are patentably distinct and, therefore, withdrawal of the rejection is solicited.

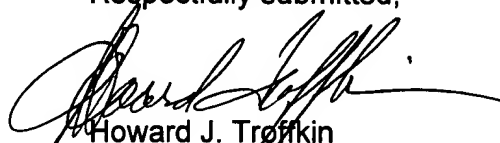
Kukes et al. is directed to a catalyst composition comprising a support having a mixture of platinum and palladium thereon. The support is composed of a Y zeolite with high sodium content (NaY) zeolite and a refractory inorganic oxide. The support is coated with palladium and platinum to provide prills of a hydrogenation catalyst useful in trickle bed reactors (See Example 16 of Kukes) .

The presently claimed catalyst is distinctly different from that taught by Kukes et al. Firstly, it is clear that the presently claimed catalyst does not use a soda Y zeolite (e.g. a sodium rich zeolite) as taught and suggested by Kukes et al. Such zeolite are distinct from that required by the presently claimed invention. Further, the claims, as presently amended, are directed to particulate material having a defined average diameter suitable for fluid cracking catalyst application while Kukes et al. provide extruded particles that would not be appropriate for such application. Finally, the presently claimed invention is directed to a catalyst composition, per se, while the cited prior art teaches that thier zeolite composite has metals coated thereon which provide catalytic activity to thus product.

* * * * *

Applicant believes that the Examiner will agree that the present claims are patentably distinct, the application is free from formal and art rejection and, therefore, the present application is in condition for allowance. Such action is respectfully solicited.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Howard J. Troffkin", written over the printed name.

Howard J. Troffkin
Attorney for Applicants
Registration No. 25,184

CLAIMS:

Claims 1-31 (Deleted).

32. (Currently Amended) A catalyst suitable for use in hydrocarbon feedstock cracking comprising particles consisting essentially of:
- i) at least greater than 70 weight percent of zeolite of Y-type selected from USY, REY, REUSY, CREY, CREUSY or mixtures thereof; and
 - ii) remainder substantially composed of an alumina sol;
- said catalyst is in the form of particulates having an average diameter of from about 50 to about 150 microns; has a kinetic conversion activity of at least about 3; and a Davison Attrition Index of less than about 20.
33. (Previously Presented) The catalyst of Claim 32 wherein the catalyst has a surface area of at least about 500 m²/g.
34. (Previously Presented) The catalyst of Claim 33 wherein the catalyst has an average bulk density of at least about 0.6 g/cc.
35. (Previously Presented) The catalyst of Claim 34 wherein the catalyst particles have a H₂O pore volume of greater than 0.32 cc/g.
36. (Previously Presented) The catalyst of Claim 32 wherein the zeolite is at least 80 weight percent of said particles.
37. (Previously Presented) The catalyst of Claim 33 wherein the zeolite is at least 80 weight percent of said particles.
38. (Previously Presented) The catalyst of Claim 34 wherein the zeolite is at least 80 weight percent of said particles.
39. (Previously Presented) The catalyst of Claim 35 wherein the zeolite is at least 80 weight percent of said particles.
40. (Deleted)

41. (Delete)
42. (Currently Amended) The catalyst of Claim ~~40-41~~32, 33, 34, 35 or 36 wherein the zeolite is CREY zeolite.
43. (Currently Amended) The catalyst of Claim ~~40-41~~32, 33, 34, 35, or 36 wherein the zeolite is REUSY zeolite.
44. (Previously Presented) The catalyst of Claim 32, 33, 34 or 35 wherein the zeolite is present in from 70 to 90 weight percent of said particles.
45. (Deleted)
46. (Deleted)
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56. (Deleted)
57. (Currently Amended) A catalyst composition useful in cracking of hydrocarbon feedstock comprising:
 - a) first particulate material composed of ~~at least~~greater than 70 weight percent zeolite ~~of Y types~~selected from USY, REY, REUSY, CREY or CREUSY

type zeolite or mixtures thereof, and the remainder substantially composed of alumina sol; wherein said first particulate material has an average diameter of from about 50 to about 150 microns; a kinetic conversion activity of at least about 3; and a Davison Attrition Index of less than about 20; and

b) second particulate material having a kinetic conversion activity of less than 3; said catalyst composition having a kinetic conversion activity of from at least about 2 to about 3.

58. (Previously Presented) The composition of Claim 57 wherein the first particulate material has a surface area of at least about 500 m²/g and a H₂O pore volume of greater than 0.32 cc/g.

59. (Previously Presented) The composition of Claim 58 wherein the first particulate material has an average bulk density of at least about 0.6 g/cc.

60. (Deleted)

61. (Deleted)

62. (Currently Amended) The composition of Claim ~~60-61~~ 57, 58, or 59 wherein the zeolite of the first particulate material is a CREY zeolite.

63. (Currently Amended) The composition of Claim ~~60-61~~ 57, 58, or 59 wherein the zeolite of the first particulate material is a REUSY zeolite.

64. (Currently Amended) The composition of Claim 57, 58 ~~or 59, 61, 62, or 63~~ wherein the second particulate material has a kinetic conversion activity of less than 1.

65. (Previously Presented) The composition of Claim 64 wherein the second particulate material is an FCC additive selected from combustion promoters, nickel passivators, vanadium passivators, sulfur reduction agents, nitrogen reduction agents or mixtures thereof.

66. (Previously Presented) The composition of Claim 64 wherein the first particle has zeolite in at least 80 weight percent of said particles.
67. (New) The composition of Claim 62 therein the composition of Claim 64 wherein the second particulate material is an FCC additive selected from combustion promoters, nickel passivators, vanadium passivators, sulfur reduction agents, nitrogen reduction agents or mixtures thereof.
68. (New) The composition of Claim 63 wherein the composition of Claim 64 wherein the second particulate material is an FCC additive selected from combustion promoters, nickel passivators, vanadium passivators, sulfur reduction agents, nitrogen reduction agents or mixtures thereof.
69. (New) The composition of Claim 62 wherein the composition of Claim 64 wherein the first particle has zeolite in at least 80 weight percent of said particles.
70. (New) The composition of Claim 62 wherein the composition of Claim 64 wherein the first particle has zeolite in at least 80 weight percent of said particles.
71. (New) The composition of Claim 63 wherein the composition of Claim 64 wherein the first particle has zeolite in at least 80 weight percent of said particles.



Effect of vanadium on USY zeolite destruction in the presence of sodium ions and steam—studies by solid-state NMR

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Abstract

The effect of deposited vanadium on the thermal destruction of ultra stable Y (USY) zeolite in the presence of sodium ions and steam was investigated by solid-state NMR. When USY zeolite containing few sodium ions was heated in a dry atmosphere, Si–OH groups, which corresponded to defect sites, and strong adsorption sites were formed by the dealumination. The former mainly caused an increase in the mean void volume per supercage and the latter originated from cationic extra framework Al in the supercages. Furthermore, in the dry atmosphere, the sodium ions inhibited the dealumination; the effect of the deposited vanadium on the structural change was not large. After the heat treatment in 100% steam, in case of USY zeolite containing few sodium ions, the crystallinity and the supercage structure hardly changed although the dealumination occurred remarkably. This process did not depend on the deposited vanadium. Data suggested that the heat treatment in 100% steam causes the framework stabilization. In case of USY zeolite containing a number of sodium ions, the synergistic effect between a few deposited vanadium ions and the sodium ions on the framework destruction in 100% steam was tremendous. We propose that the deposited vanadium functions as vanadic acid and catalyzes the conversion of the sodium ions into NaOH. Thus, an increase in the NaOH content promotes the ‘dissolution’ of the zeolite crystal, i.e. the framework destruction. In addition, when the sample containing both a few vanadium ions and a number of sodium ions was heated in 100% steam, the supercage was plugged partially. We believe that the blockage compounds in the supercage are sodium vanadates.

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Keywords: USY zeolite; Solid-state NMR; Vanadium deposition; Dealumination; Framework destruction; Heat treatment

1. Introduction

Recently, the demand for heavy petroleum products has been reduced year by year, so fluid catalytic cracking (FCC) processes in refineries tend to be adapted

for heavier distillates such as atmospheric residues. Indeed, many FCC processes for atmospheric residues have been constructed in the world, and vacuum gas oils mixed with atmospheric residues have been treated in many classical FCC processes. In this case, it is well known that metals (Ni, V, Na, Fe, etc.) in the residues are gradually deposited on FCC catalyst particles during the process and exert a harmful influence on the cracking activity and selectivity of the catalysts [1–4]. In general, during the FCC processes, not only the

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metal deposition but also some coke formation occur along with the hydrocarbon cracking reaction in the catalyst particles containing ultra stable Y (USY) zeolite as a major active component. For the purpose of the coke removal, which is called a regeneration process, the catalyst particles are calcined under severe hydrothermal conditions (temperature: 973–1073 K, total pressure: 0.1–0.2 MPa, partial steam pressure: about 20%). In this case, a structural change such as a dealumination of the USY zeolite occurs during the regeneration, and the Brønsted acid sites which play an important role in the cracking reaction have decreased in number. Although it is supposed that the vanadium deposited on the USY zeolite affects the dealumination and the framework destruction, this mechanism has not been fully clarified yet. Occelli reported that $\text{H}_4\text{V}_2\text{O}_7$ resulted from the reaction between V_2O_5 and H_2O and destroyed the USY zeolite framework [5,6]. On the contrary, based on the thermodynamic data of Yanopolous [7], Wormsbecher et al. indicated that volatile H_3VO_4 , analogous to H_3PO_4 , was produced from V_2O_5 and H_2O , and catalyzed some hydrolysis of the framework [8]. In this respect, Pine reported from the kinetic analysis that both the vanadium and sodium ions synergistically acted as catalysts on the framework destruction [9]. Trujillo et al. supported Pine's result and also explained that the synergistic effect between the vanadium and sodium ions on the framework destruction was enormous, but they did not clarify the mechanism of the synergistic effect enough [10]. Masuda et al. previously reported that an eutectic resulted from an interaction between the vanadium and zeolite matrix elements and that its melting point was lowered when sodium ions were present [11]. However, Pine denied that the synergistic effect was caused by a decrease in the melting point of the eutectic because steam was necessary for the framework destruction related with the deposited vanadium. In other words, if the eutectic formation were the essential operative mechanism, the framework destruction should take place in the atmosphere not containing H_2O . Recently, Xu et al. proposed two pathways with respect to the framework destruction by the vanadium deposition [12,13]. According to them, in the case of a few sodium ions in USY zeolite, most of the framework destruction was caused by the hydrolysis and the effect of the vanadium was small at the normal content (0.4 wt.%). When the content of sodium ions

increased, however, the framework destruction originated from NaOH formation, which occurred due to a reaction between sodium ions with H_2O in the atmosphere and was promoted by the deposited vanadium. This proposal is closely related with the previous report that the solubility of quartz was proportional to the base concentration under the hydrothermal condition [14].

The purpose of this study is to clarify the effect of the deposited vanadium on the dealumination and the framework destruction of USY zeolite in the presence of sodium ions and steam. Thus, we prepared several USY zeolite samples treated at high temperatures with or without vanadium, sodium ions and in the dry atmosphere or 100% steam, and we analyzed their structure by various solid-state NMR spectroscopies including ^{129}Xe NMR. It is known that ^{129}Xe NMR is a powerful technique for analysis of porous materials such as USY zeolite [15,16]. XRD is also a useful technique as a complement to the solid-state NMR analyses when the mechanisms of the dealumination and the framework destruction are discussed in detail.

2. Experimental

2.1. Sample preparation

The reference USY zeolite in this study (USY-R) was a sample obtained from an acid treatment of a commercial USY zeolite HSZ-331HSA (Tosoh). HSZ-331HSA was prepared by an unknown 'ultra stable treatment' previously, and a certain amount of both extra framework aluminum (EFAI) and sodium ions have been detected. The purpose of the acid treatment was to remove the ions completely. Thus, 200 g of HSZ-331HSA were stirred in 2.5 l of 0.5 mol/dm³ ammonium sulfate solution including 25 g of H_2SO_4 at 340 K for 4 h; powder was filtered out of the solution and dried at 383 K overnight to prepare USY-R. A vanadium impregnation method was based on the procedure reported by Mitchell [17]. Namely, the sample was dried at 673 K for 4 h for the purpose of removal of adsorbed H_2O , and then impregnated using a cyclohexane solution of a vanadium naphthenate; finally the material was calcined at 773 K for 5 h. The vanadium-impregnated USY-R was denoted as V-USY. And USY-R was stirred in 0.2 mol/dm³

Table 1
Chemical analysis of the USY zeolites before heating by ICP-AES

Sample	Si (wt.%)	Al (wt.%)	Na (wt.%)	Si/Al ratio (mol/mol)	V (wt.%)
HSZ-331HSA	27	8.5	0.16	3.1	n.d.
USY-R	31	6.6	0.07	4.5	n.d.
V-USY	33	6.6	0.04	4.8	0.17
Na-USY	30	5.6	2.40	5.2	n.d.
V-Na-USY	32	5.9	2.50	5.2	0.15

sodium acetate solution at 343 K for 3 h to exchange H^+ for Na^+ once more. The prepared sample was denoted as Na-USY. The vanadium impregnation into Na-USY was done by the same procedure as mentioned above. The vanadium-impregnated Na-USY was denoted as V-Na-USY. Table 1 shows the elemental analysis of these samples by ICP-AES. Furthermore, in order for us to investigate the effect of the calcination with the above procedure, both USY-R and Na-USY were dried and calcined without the vanadium impregnation. These two samples prepared were denoted as 'C-USY-R' and 'C-Na-USY', respectively.

In this study, USY-R, V-USY, Na-USY and V-Na-USY were treated thermally by the following procedure. After H_2O adsorbed on the sample was removed by heating at 573 K for 1 h in the dry atmosphere, the heating temperature was elevated by 1073 K at the rate of 5 K/min; then the sample was heated in the dry atmosphere or 100% steam at 1073 K for 1 h. In addition, a typical NaY (Aldrich, Si/Al = 2.2, unit cell size: 2.467 nm), which was called 'LZY-52', was used for comparison.

2.2. Characterization

2.2.1. Solid-state NMR

All solid-state NMR spectra were measured at the ambient temperature with a JNM-CMX-400 spectrometer (JEOL). The magic angle spinning (MAS) method, a zirconia rotor and the sample absorbing enough H_2O were used in ^{29}Si and ^{27}Al measurements. ^{29}Si MASNMR spectra were observed at 79.524 MHz. The number of accumulations between 500 and 2000, a MAS speed of 3.5 kHz and a recycle time of 10 s were used. A flip angle of pulse width was set as $\pi/4$ with a single pulse sequence not us-

ing cross polarization (CP), while the width was $\pi/2$ with CP sequence. In the CP experiment, a contact time of 5 ms was used. The ^{29}Si chemical shift of polydimethylsilane used as a secondary standard was taken to equal -34 ppm in the high field from liquid tetramethylsilane. A framework Si/Al ratio was calculated by deconvoluting the ^{29}Si MASNMR spectrum with a single pulse sequence. ^{27}Al MASNMR spectra were observed at 104.309 MHz with a single pulse sequence. A pulse width of $\pi/12$ flip angle, a recycle time of 2 s, 400 accumulations and a MAS speed of 12 kHz were used. The ^{27}Al chemical shift was quoted from 1 mol/dm³ aqueous solution of $Al(NO_3)_3$.

Prior to measurement of ^{129}Xe NMR, the following experiments were carried out. The sample was dried at 673 K in a homemade NMR glass tube for 4 h under 10^{-2} Pa. Then the xenon adsorption isotherm on the dry sample, which followed the Henry equation, was measured at the ambient temperature. After the isotherm measurement, NMR spectra of xenon adsorbed under several equilibrium pressures were observed at 110.726 MHz with a single pulse sequence. A pulse width of $\pi/4$ flip angle, a recycle time of 1 s and the number of accumulations between 500 and 40,000 were used without MAS. The chemical shifts were determined relative to xenon gas extrapolated to zero pressure [18]. In this respect, Ito and Fraissard showed that the chemical shift δ of adsorbed xenon could be expressed as the sum of several terms [19]. In the case of USY zeolite, the xenon whose atomic diameter is 0.44 nm cannot get into any cages except a supercage, so that δ depends on collisions between the xenon and the other atoms only in the supercage [16,20]:

$$\delta = \delta_0 + \delta_S + \delta_{Xc} + \delta_E$$

δ_0 is the reference, the chemical shift of gaseous xenon extrapolated to zero pressure; δ_S the term which depends on the diffusibility of xenon; δ_{Xc} corresponds to the density of xenon in the supercage; and δ_E represents the contribution of adsorption sites stronger than H^+ or Na^+ , such as bivalent cations. In practice, the important information is obtained from the $\delta = f(N)$ curve, where N is the amount of xenon adsorbed per unit weight of the sample. It is known that δ_S , the intercept of the linear section of the $\delta = f(N)$ curve, depends on the pore structure, for example, the supercage arrangement; $\partial\delta/\partial N$, the slope of the linear

section of the $\delta = f(N)$ curve, is proportional to the reciprocal of the supercage void volume of the sample; and the curvature of the $\delta = f(N)$ curve corresponds to δ_E and is increased with the number of the strong adsorption sites.

2.2.2. XRD

Powder XRD patterns were measured with a RINT-2500V diffractometer (Rigaku). The unit cell size and the relative XRD intensity representative of crystallinity were determined according to the ASTM methods D3942-91 and D3906-91, respectively. The crystallinity of NaY was considered as a reference in this paper.

3. Results and discussion

3.1. Vanadium impregnation

Fig. 1 shows ^{27}Al MASNMR spectra of USY-R, C-USY-R and V-USY, which contained few sodium ions (<0.1 wt.%). In the case of Y zeolite, it is well known that a peak at about 60 ppm and one at about 0 ppm should be assigned to 4-coordinated Al and 6-coordinated Al, respectively. Compared with

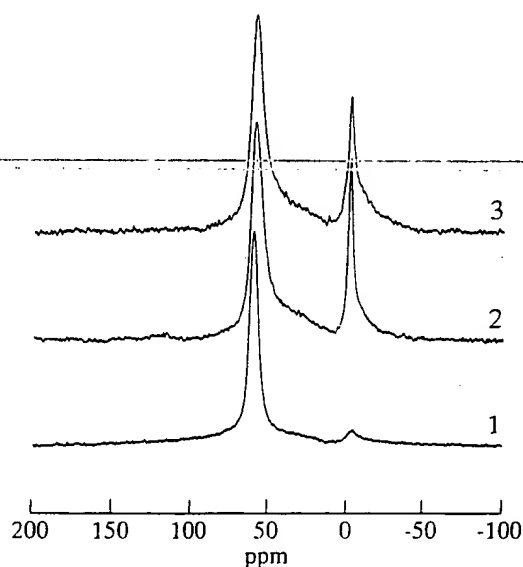


Fig. 1. ^{27}Al MASNMR spectra of the USY zeolites containing few sodium ions (<0.1 wt.%): (1) USY-R; (2) C-USY-R; (3) V-USY.

Table 2

XRD analysis and framework Si/Al ratios obtained from ^{29}Si MASNMR spectra of the USY zeolites

Sample	Unit cell size (Å)	Crystallinity (relative peak intensity) (%) ^a	Framework Si/Al ratio (mol/mol)
USY-R	24.53	110	5.7
C-USY-R	24.47	105	8.0
V-USY	24.46	103	8.0
Na-USY	24.51	105	5.7
C-Na-USY	24.50	106	5.7
V-Na-USY	24.50	104	6.0

^a The relative peak intensity of NaY zeolite was taken as 100%.

USY-R, the peak intensity at 0 ppm increased remarkably in C-USY-R and V-USY. This result suggests that a number of 6-coordinated Al, which generally corresponded to EFAl, were present in both C-USY-R and V-USY. Therefore, the dealumination occurred due only to the calcination with the vanadium impregnation, but independent of the vanadium addition. The ^{27}Al MASNMR analysis almost agreed with the unit cell size listed in Table 2 and single pulse ^{29}Si MASNMR spectra shown in the lower part of Fig. 2. Thus, the unit cell size of V-USY was smaller than that of USY-R and almost equal to that of C-USY-R. According to ^{29}Si MASNMR spectra with a single pulse sequence, the peak at -89 ppm assigned to $\text{Si}(3\text{Al})$ in Q^4 (SiO_4) almost vanished in both V-USY and C-USY-R, different from USY-R. Framework Si/Al ratio of V-USY was also larger than that of USY-R and equal to that of calcined USY-R (Table 3). All of these results can be regarded as the dealumination rate. Consequently, it is clear that the dealumination with the vanadium impregnation was affected only by the calcination and not by the deposited vanadium itself.

^{29}Si CP/MASNMR spectra are shown in the upper part of Fig. 2. In the case of Y zeolite, ^{29}Si

Table 3

XRD analysis and framework Si/Al ratios of the USY zeolites heated in dry atmosphere

Sample	Unit cell size (Å)	Crystallinity (relative peak intensity) (%) ^a	Framework Si/Al ratio (mol/mol)
USY-R	24.41	100	9.5
V-USY	24.39	98	10.4
Na-USY	24.48	105	6.9
V-Na-USY	24.47	101	7.1

^a The relative peak intensity of NaY zeolite was taken as 100%.

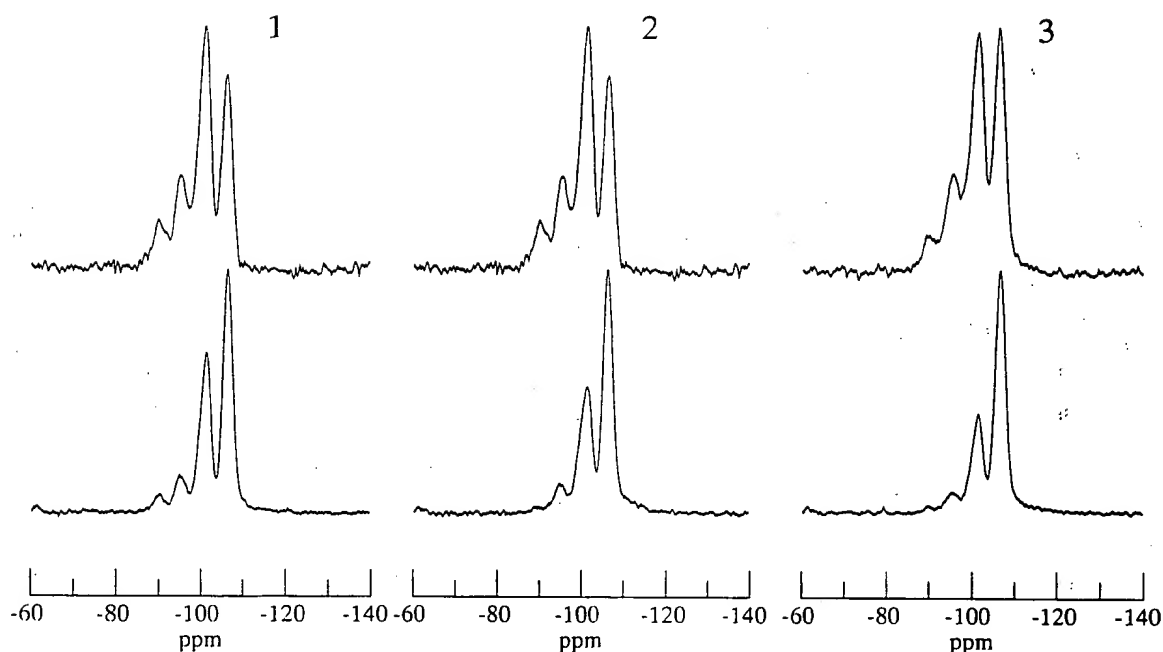


Fig. 2. ^{29}Si MASNMR spectra with single pulse (lower spectra) or cross polarization (upper spectra) of USY zeolite samples containing few sodium ions (<0.1 wt.%): (1) USY-R; (2) C-USY-R; (3) V-USY.

CP/MASNMR peaks at -101 , -95 and -89 ppm are assigned to Q^3 ($\equiv \text{SiOH}$), Q^2 ($\equiv \text{Si}(\text{OH})_2$) and Q^1 ($-\text{Si}(\text{OH})_3$), respectively, but overlap those assigned to $\text{Si}(n\text{Al})$ ($n = 1-3$) in Q^4 detected by a single pulse sequence. Thus, when Q^n ($n = 1-3$) peaks in ^{29}Si CP/MASNMR spectra get relatively large in comparison with single pulse ^{29}Si MASNMR spectra, a number of Si-OH groups are present in zeolite framework and outer surface. According to ^{29}Si CP/MASNMR spectra of both C-USY-R and V-USY, the peak intensity of Q^n , especially Q^1 , increased remarkably, different from USY-R. This result indicates that more Si-OH groups were included in both C-USY-R and V-USY than in USY-R. Such results suggest that the calcination with the vanadium impregnation caused the formation of Si-OH groups.

Fig. 3 shows $\delta = f(N)$ curves of NaY, USY-R, C-USY-R and V-USY obtained from the ^{129}Xe NMR measurements. In C-USY-R and V-USY, for the smaller N , the curvature of the curve became gradually larger, so that there were some strong absorption sites such as bivalent cations in the supercage. C-USY-R, however, did not contain any elements

except Al, which formed bivalent cations, and the vanadium content in V-USY was <0.2 wt.%. Thus, it is supposed that these strong adsorption sites were caused by cationic EFAI such as AlOH^{2+} [21], which resulted from the dealumination with the vanadium impregnation and did not originate from the deposited vanadium. This mechanism, including the formation of Si-OH groups mentioned above, will be discussed in the following section.

Fig. 4 shows ^{27}Al MASNMR spectra of Na-USY, C-Na-USY and V-Na-USY, which contained a number of sodium ions (about 2.4 wt.%). Compared with Na-USY, the peak assigned to 6-coordinated Al got a little larger in C-Na-USY and V-Na-USY. The peak intensity in these samples, however, was much smaller than that in the heated samples containing few sodium ions, i.e. C-USY-R and V-USY (Fig. 1). This result indicates that the sodium ions inhibited the dealumination with the vanadium impregnation. The ^{27}Al MASNMR analysis almost agreed with the unit cell size (Table 2), ^{29}Si MASNMR spectra (Fig. 5), framework Si/Al ratio (Table 2) and the slope of $\delta = f(N)$ curves (Fig. 6). According to these analyses, Na-USY,

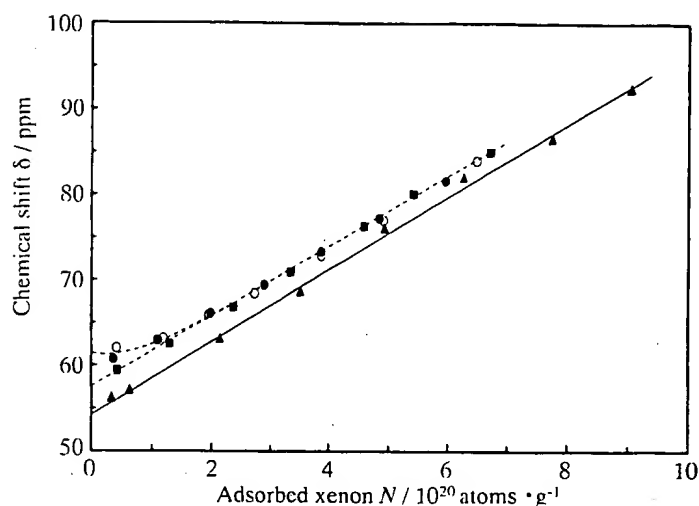


Fig. 3. $\delta = f(N)$ curves obtained from ^{129}Xe NMR of the USY zeolites containing few sodium ions (<0.1 wt.%): (▲) NaY; (■) USY-R; (○) C-USY-R; (●) V-USY.

C-Na-USY and V-Na-USY were almost equal in the framework structure; this result has supported the above suggestion, i.e. the inhibition of dealumination by the sodium ions at the vanadium impregnation.

3.2. Heat treatment in the dry atmosphere

^{27}Al MASNMR spectra, ^{29}Si MASNMR spectra, XRD analysis and framework Si/Al ratio of USY zeolites heated in the dry atmosphere are shown in Figs. 7, 8 and Table 3, respectively. From ^{27}Al MASNMR spectra, the broad peak at around 0 ppm assigned to 6-coordinated Al appeared strongly in USY-R and V-USY, while it almost vanished in Na-USY and V-Na-USY. From ^{29}Si MASNMR spectra with a single pulse sequence (lower part in Fig. 8), the peaks at -89, -95 and -101 ppm assigned to Si(3Al), Si(2Al) and Si(1Al), respectively, got smaller in USY-R and V-USY, while they appeared clearly in Na-USY and V-Na-USY. In addition, there was only a small difference in the unit cell size and framework Si/Al ratio between USY-R and V-USY or between Na-USY and V-Na-USY. These results show that the dealumination rate determined by the heat treatment in the dry atmosphere depends on the sodium ion content in USY zeolite. Furthermore, from ^{29}Si CP/MASNMR spectra (upper part in Fig. 8), the peaks assigned to Q^3 , Q^2 and Q^1 , which included Si-OH groups, got stronger in USY-R and V-USY than in Na-USY and V-Na-USY. This result indicates that Si-OH groups were formed more easily in H^+ -type USY zeolite than in Na^+ -type. This mechanism is similar to the formation of Si-OH groups by the calcination with

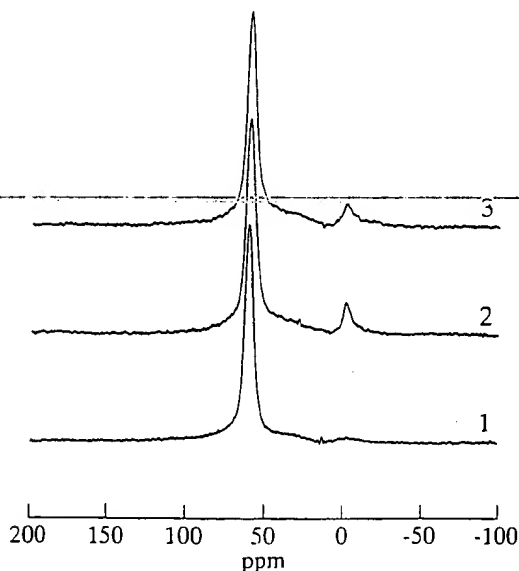


Fig. 4. ^{27}Al MASNMR spectra of the USY zeolites containing a number of sodium ions (2.4 wt.%) before or after vanadium impregnation: (1) Na-USY; (2) C-Na-USY; (3) V-Na-USY.

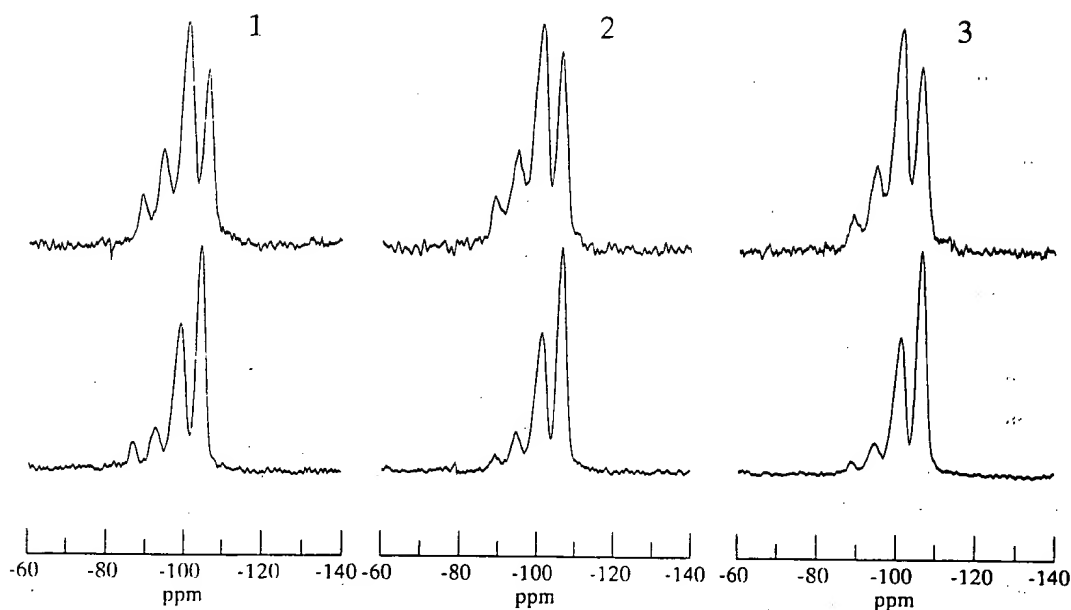


Fig. 5. ^{29}Si MASNMR spectra with single pulse (lower spectra) or cross polarization (upper spectra) of the USY zeolites containing a number of sodium ions (2.4 wt.%): (1) Na-USY; (2) C-Na-USY; (3) V-Na-USY.

the vanadium impregnation, as discussed above. We suppose that these Si–OH groups originated from the defect sites in the zeolite framework.

Fig. 9 shows $\delta = f(N)$ curves of the USY zeolites heated in the dry atmosphere. The slope of the

linear section of $\delta = f(N)$ curve ($N > 3$), $\partial\delta/\partial N$, of V-USY was almost equal to that of USY-R and smaller than that of Na-USY and V-Na-USY. As mentioned above, $\partial\delta/\partial N$ is proportional to the reciprocal of the supercage void volume, so the supercage void volume

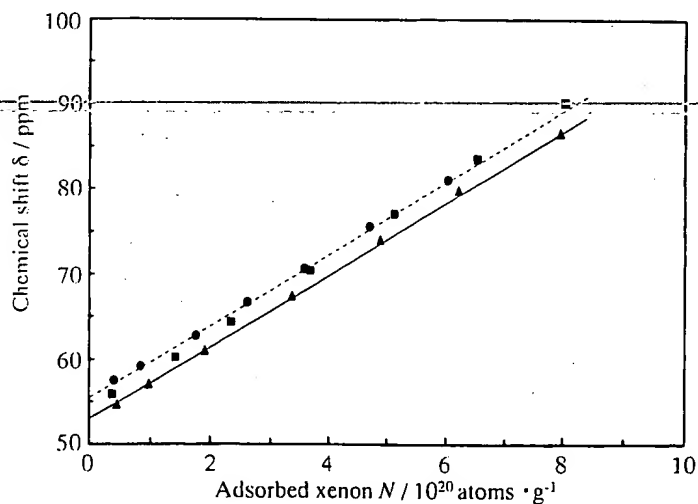


Fig. 6. $\delta = f(N)$ curves obtained from ^{129}Xe NMR spectra of the USY zeolites containing a number of sodium ions (2.4 wt.%): (\blacktriangle) Na-USY; (\blacksquare) C-Na-USY; (\bullet) V-Na-USY.

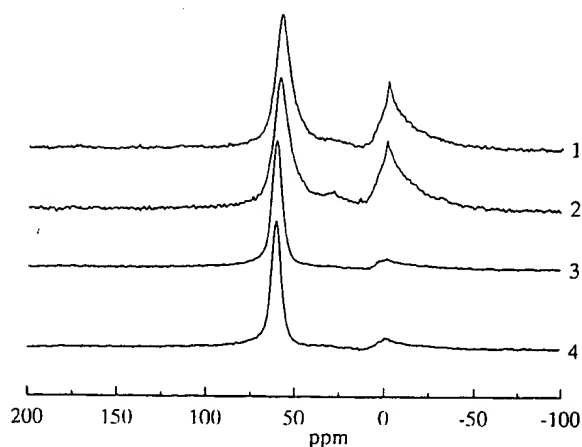


Fig. 7. ^{27}Al MASNMR spectra of the USY zeolites heated in the dry atmosphere: (1) USY-R; (2) V-USY; (3) Na-USY; (4) V-Na-USY.

of V-USY was almost equal to that of USY-R and was larger than that of Na-USY and V-Na-USY. However, there was little difference in crystallinity among these samples (Table 3). In this case, the crystallinity can be estimated at the number of the supercages in USY zeolite; these samples were almost equal in the number of the supercages. The supercage void volume can be considered as the product of the number of the supercages multiplied by the mean void volume per supercage; therefore, the mean void volume per supercage of V-USY was almost equal to that of USY-R and larger than that of Na-USY and V-Na-USY. According to ^{29}Si CP/MASNMR spectra of the heated samples, more Si–OH groups, which mainly originated from the defect sites, were included in both USY-R and V-USY than in both Na-USY and V-Na-USY. Thus, we suppose that most of the growth of the mean void volume per supercage was caused by the formation of the defect sites in the supercage.

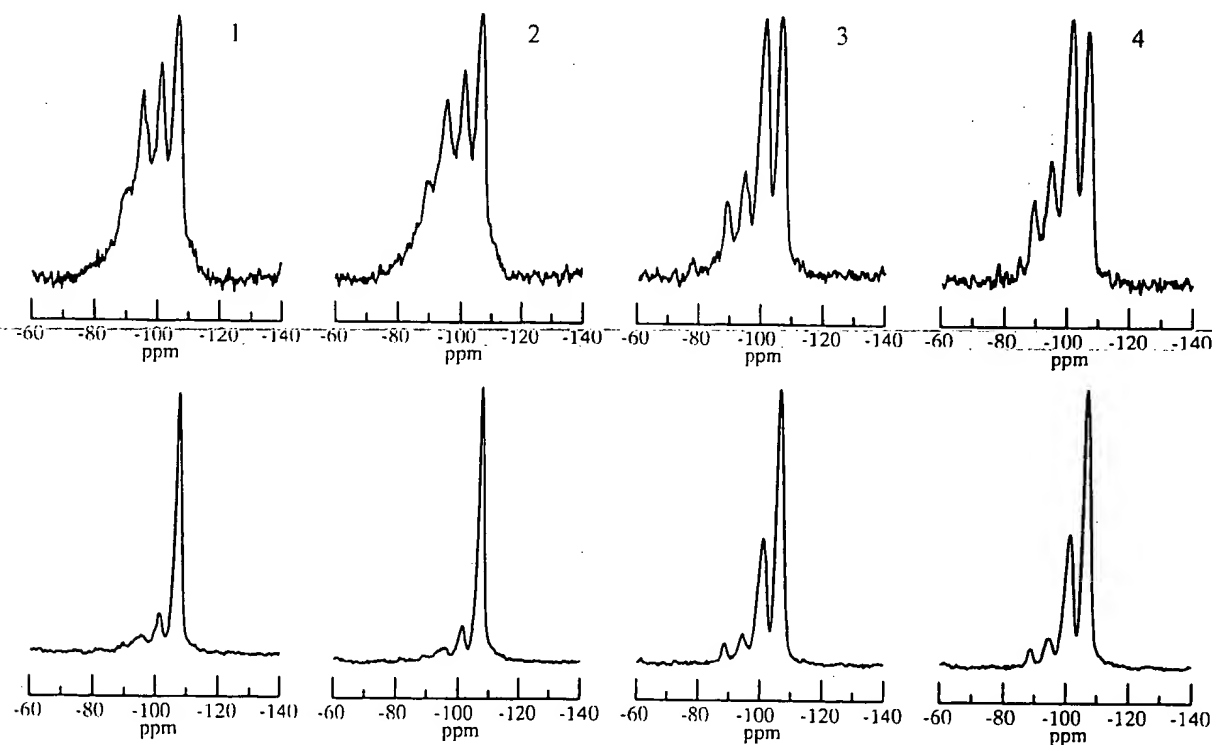


Fig. 8. ^{29}Si MASNMR spectra with single pulse (lower spectra) or cross polarization (upper spectra) of the USY zeolites heated in the dry atmosphere: (1) USY-R; (2) V-USY; (3) Na-USY; (4) V-Na-USY.

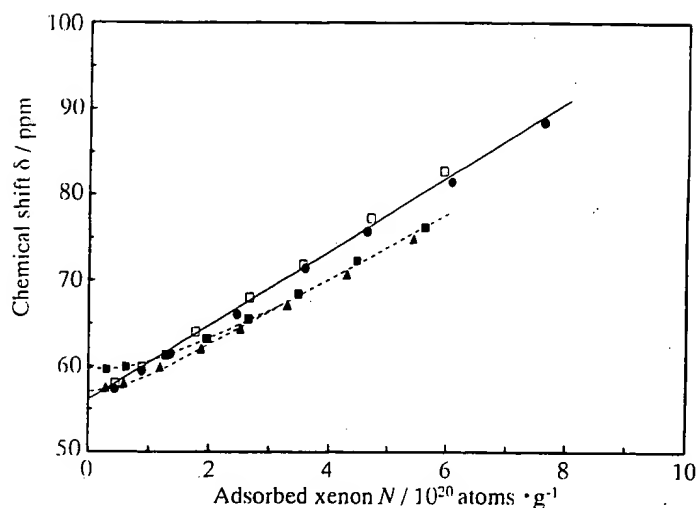


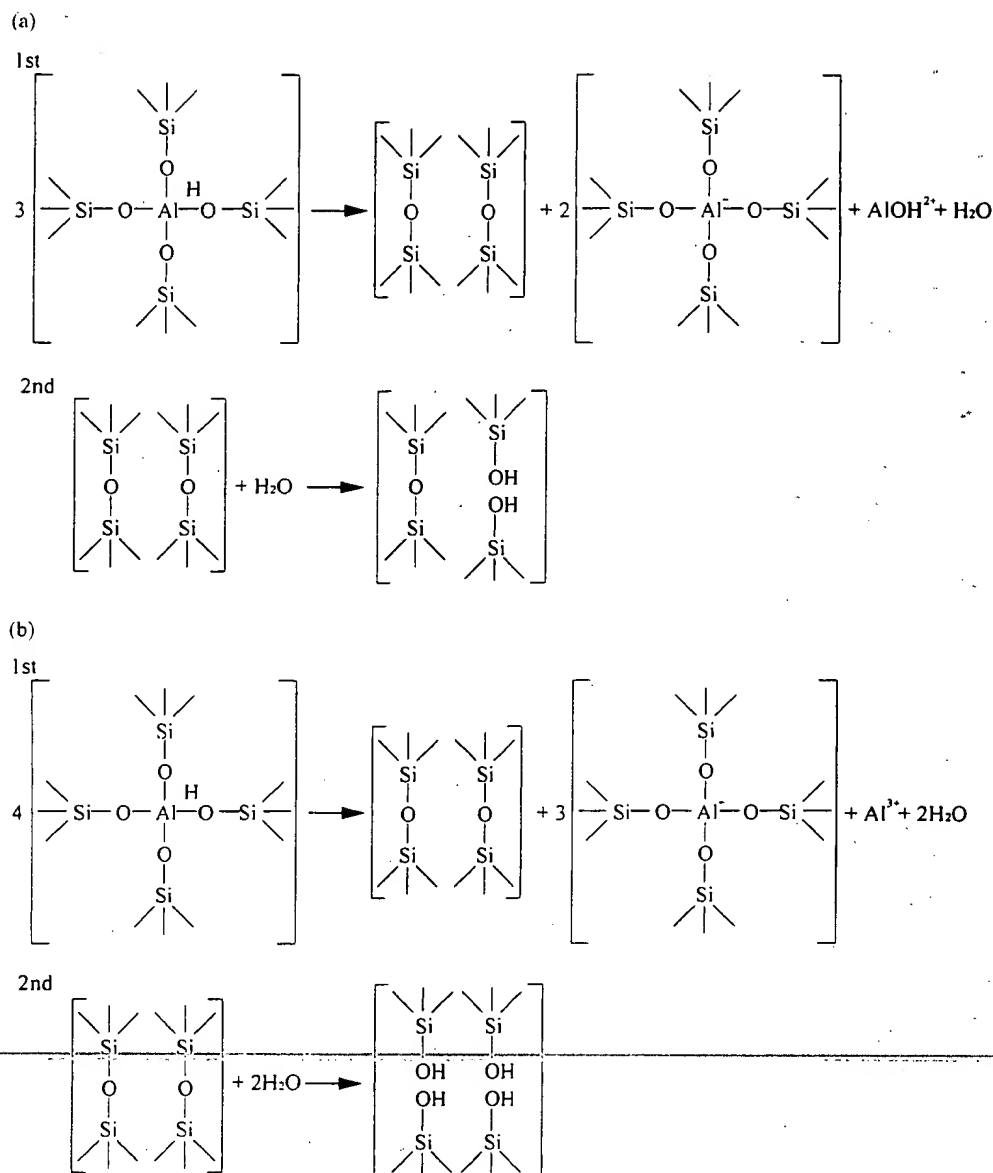
Fig. 9. $\delta = f(N)$ curves obtained from ^{129}Xe NMR spectra of the USY zeolites heated in the dry atmosphere: (\blacktriangle) USY-R; (\blacksquare) V-USY; (\bullet) Na-USY; (\square) V-Na-USY.

At low amounts of adsorbed xenon ($N < 3$), the $\delta = f(N)$ curves of both USY-R and V-USY varied non-linearly, different from Na-USY and V-Na-USY. This result indicates that the strong adsorption sites such as bivalent cations were present in the supercages of USY-R and V-USY. In other words, the heat treatment caused the formation of these sites. As mentioned in the above section, in USY-R and V-USY the content of the elements which formed bivalent cations was extremely small except for Al, so these strong adsorption sites were caused by cationic EFAl such as AlOH^{2+} [21], which resulted from the dealumination accompanied by the heat treatment in the dry atmosphere. If one considers the formation of both the Si–OH groups and the cationic EFAl in the supercage of the sample containing few sodium ions, the dealumination mechanism shown in Scheme 1 seems plausible [16]. Thus, cationic EFAl, H_2O and Si–O–Si groups are formed by a reaction among more than three framework Al ions exchanged to H^+ themselves. Then Si–OH groups originate from a reaction between Si–O–Si groups and formed H_2O . In this respect, Barrer and Klinowski reported the first reaction previously and did not display the second reaction involving the formation of Si–OH groups [22]. Taking into account the ^{29}Si CP/MAS NMR analysis, however, we believe that the second reaction is also valid.

In addition, the effect of the deposited vanadium on the dealumination in the dry atmosphere was not large, because the difference in those analyses was small regardless of whether the vanadium was contained or not. As mentioned above, the dealumination with the vanadium impregnation into the USY zeolite containing few sodium ions was mostly caused by the calcination and was not concerned with the deposited vanadium directly. Therefore, it is suggested that in the dry atmosphere the deposited vanadium hardly affects the dealumination which occurs following Scheme 1.

3.3. Heat treatment in 100% steam

The XRD patterns of the USY zeolites heated in 100% steam are shown in Fig. 10. XRD peaks originating from a faujasite structure decreased remarkably in the USY zeolites containing a number of sodium ions (Na-USY, V-Na-USY), while the peaks hardly varied in the USY zeolites containing few sodium ions (USY-R, V-USY). This result indicates that the sodium ions promoted the framework destruction under this hydrothermal condition. Furthermore, the crystallinity of V-Na-USY, obtained from the XRD pattern and shown in Table 4, became about 60% of that of Na-USY. Such data suggested that the synergistic effect between the sodium ions and the



Scheme 1. Mechanism for formation of cationic EFAI and Si-OH groups in USY zeolite by heat treatment in the dry atmosphere: (a) three framework Al reaction; (b) four framework Al reaction [16,22].

deposited vanadium on the framework destruction in 100% steam was tremendous, which agrees with the previous studies [9,10,12,13]. And in the case of the sample containing few sodium ions, the deposited vanadium did not influence on the framework destruction and the crystallinity was mostly maintained. This result also agrees with what Xu et al. reported [12,13].

Fig. 11 shows ^{27}Al MASNMR spectra of the USY zeolites after the heat treatment in 100% steam. In USY-R and V-USY, not only a peak at about 0 ppm assigned to 6-coordinated Al but also one at about 30 ppm assigned to 5-coordinated Al, which also corresponded to EFAI, appeared. On the other hand, neither a peak from 5-coordinated Al nor one from

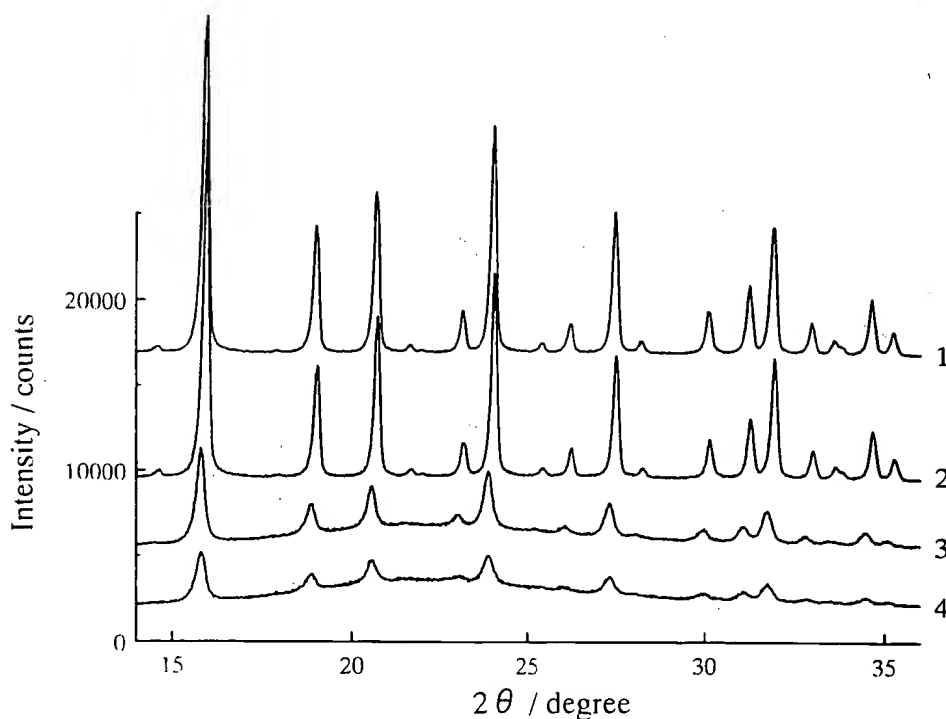


Fig. 10. XRD patterns of the USY zeolites heated in 100% steam: (1) USY-R; (2) V-USY; (3) Na-USY; (4) V-Na-USY.

6-coordinated Al was observed in the spectra of either Na-USY or V-Na-USY. In practice, according to the decrease in the unit cell size due to the heat treatment in 100% steam (Table 4), a number of EFAI were included in Na-USY and V-Na-USY. Thus, the disappearance of the peaks corresponding to EFAI mostly resulted from antisymmetric distortion of the EFAI structure. In other words, the highly distorted EFAI possessed a large second order quadrupolar effect, which broadened the peak remarkably and was not removed by only MAS under this experimental condition. This result is closely related with the low

crystallinity of Na-USY and V-Na-USY. Furthermore, in V-Na-USY the peak assigned to 4-coordinated Al shifted about 10 ppm to high magnetic field; therefore, they were not incorporated into the framework enough.

Table 4
XRD analysis of the USY zeolites heated in 100% steam

Sample	Unit cell size (Å)	Crystallinity (relative peak intensity) (%) ^a
USY-R	24.33	98
V-USY	24.30	93
Na-USY	24.38	32
V-Na-USY	24.37	19

^a The relative peak intensity of NaY zeolite was taken as 100%.

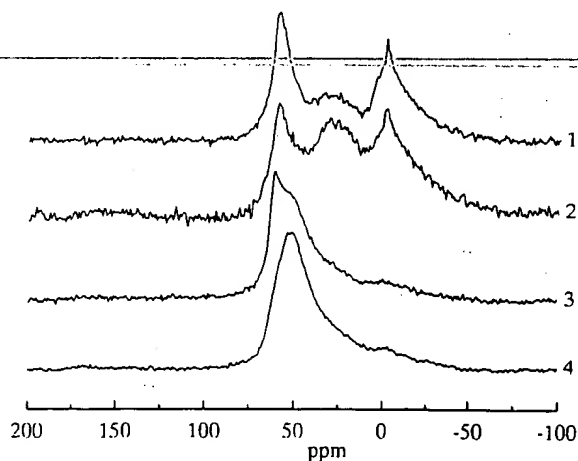


Fig. 11. ²⁷Al MASNMR spectra of the USY zeolites heated in 100% steam: (1) USY-R; (2) V-USY; (3) Na-USY; (4) V-Na-USY.

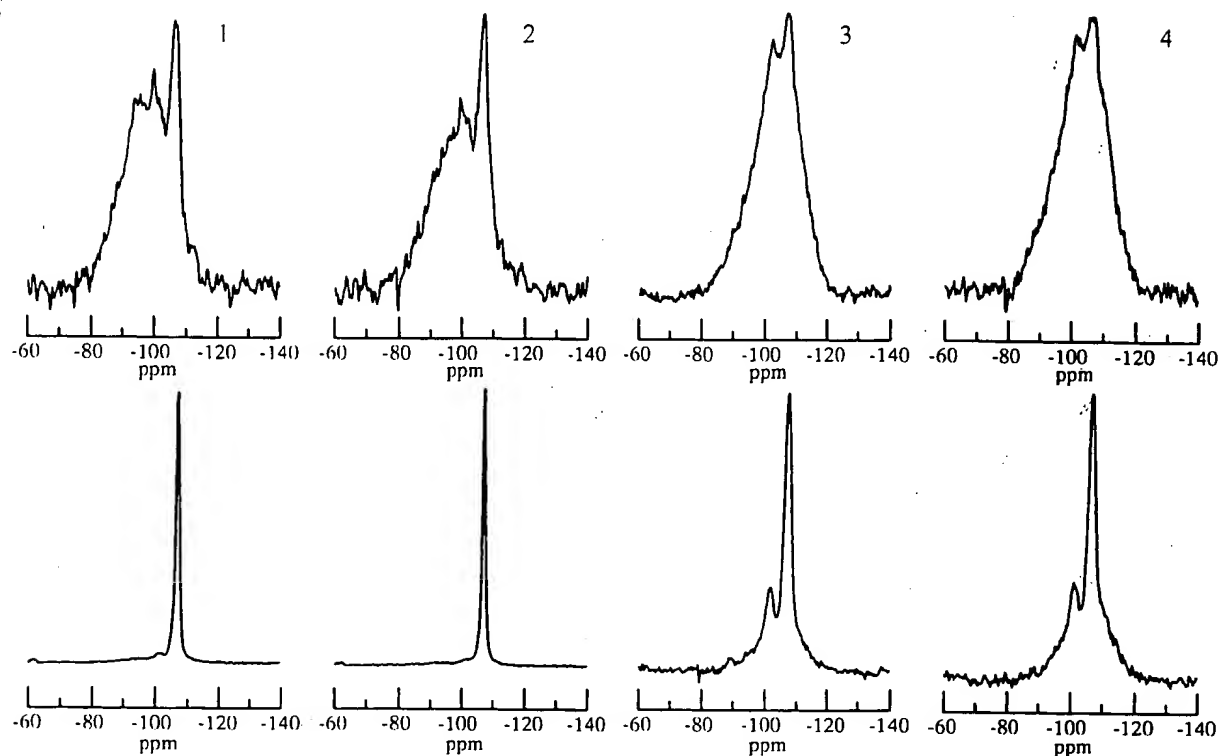


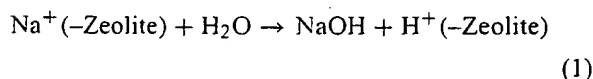
Fig. 12. ^{29}Si MASNMR spectra with single pulse (lower spectra) or cross polarization (upper spectra) of the USY zeolites heated in 100% steam: (1) USY-R; (2) V-USY; (3) Na-USY; (4) V-Na-USY.

Fig. 12 shows ^{29}Si MASNMR spectra of these zeolites heated in 100% steam. In USY-R and V-USY containing few sodium ions, a sharp peak at about -107 ppm assigned to Si(0Al) appeared, while one at about -101 ppm assigned to Si(1Al) almost vanished from the NMR spectra with a single pulse sequence (lower part in Fig. 12). Before the heat treatment in 100% steam, the peaks corresponding not only to Si(1Al) but also to Si(2Al) appeared clearly (lower part in Fig. 2), so the dealumination remarkably occurred, as discussed above. With a little decrease in the crystallinity of the heated samples (Table 4), however, the crystalline arrangements of the framework structure in USY-R and V-USY were almost maintained after the heat treatment in 100% steam. In addition, there was little difference in the two kinds of the ^{29}Si MASNMR spectra between USY-R and V-USY. Taking into account the unit cell size and the crystallinity of the heated USY zeolites containing few sodium ions, we believe that the deposited vanadium

hardly affects the dealumination and the framework destruction during the heat treatment in 100% steam.

In Na-USY and V-Na-USY containing a number of sodium ions, the peak corresponding to Si(1Al) appeared relatively clear in the NMR spectra with a single pulse sequence (lower part in Fig. 12), different from USY-R and V-USY. This result indicates that, after the heat treatment in 100% steam, the dealumination rates of both Na-USY and V-Na-USY were smaller than those of both USY-R and V-USY; the result agrees with the fact that the unit cell sizes, which can be considered as another index of the dealumination rate, of these samples were larger than those of USY-R and V-USY (Table 4). Furthermore, the broad peak corresponding to an amorphous phase appeared relatively large in Na-USY and V-Na-USY. According to ^{29}Si CP/MASNMR spectra of Na-USY and V-Na-USY (upper part in Fig. 12), a peak assigned to Q^4 almost overlapped one assigned to Q^3 , while in USY-R and V-USY the peak assigned to Q^4

separated from the other peaks. This result indicates that the Q^4 structure of Na-USY and V-Na-USY got more irregular than that of USY-R and V-USY. These also agree with the fact that the crystallinity values of Na-USY and V-Na-USY were much smaller than those of USY-R and V-USY. From these analyses, one concludes that the effect of the sodium ions on the dealumination and the framework destruction in 100% steam can be expressed by the two following factors: (1) the sodium ions promote the framework destruction remarkably and (2) they inhibit the dealumination of the framework left after the heat treatment in 100% steam. Although these factors seem to be contradictory to each other, this problem can be solved by the following explanation. With respect to the first factor, based on the previous report that the solubility of quartz was directly proportional to the base concentration under hydrothermal condition [14], USY zeolite crystal dissolves gradually in 100% steam containing the sodium ions, i.e. an alkaline solution. In other words, when steam is supplied continually, the following reaction occurs:



So the NaOH content in the crystal gets high and as a result the 'dissolution' of the zeolite crystal which can be considered as the framework destruction oc-

Table 5

^{129}Xe NMR $\delta = f(N)$ curve analysis of the USY zeolites heated in 100% steam

Sample	The slope $\partial\delta/\partial N$ of linear section of $\delta = f(N)$ curve (ppm g/10 ²⁰ atoms)	The intercept δ 's of linear section of $\delta = f(N)$ curve (ppm)
NaY	4.2	55
USY-R	4.6	51
V-USY	4.7	52
Na-USY	13.5	64
V-Na-USY	39.1	64

curs. And the second factor can be explained by the assumption that in the crystal diffusion of H_2O is slow and so the H_2O content is inhomogeneous. Namely, in the surface region of the crystal the H_2O content is high and so reaction (1) occurs rapidly, while in the center region of the crystal it is low and so reaction (1) seldom occurs. The latter mechanism is closely related with the suggestion that the sodium ions inhibit the dealumination with the heat treatment in the dry atmosphere, following Scheme 1 as mentioned above.

The $\delta = f(N)$ curves of the USY samples heated in 100% steam and the analyses, i.e. δ 's and $\partial\delta/\partial N$, of the $\delta = f(N)$ curves are shown in Fig. 13 and Table 5, respectively. $\partial\delta/\partial N$ of USY-R and V-USY was nearly equal to that of NaY, so there was little difference in the supercage void volume among these

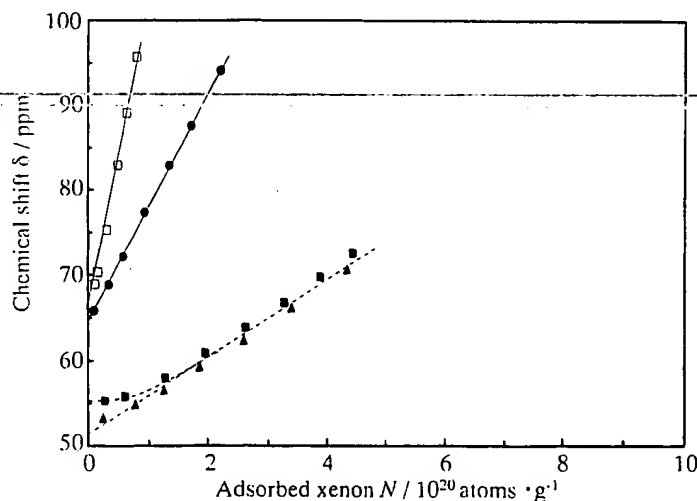
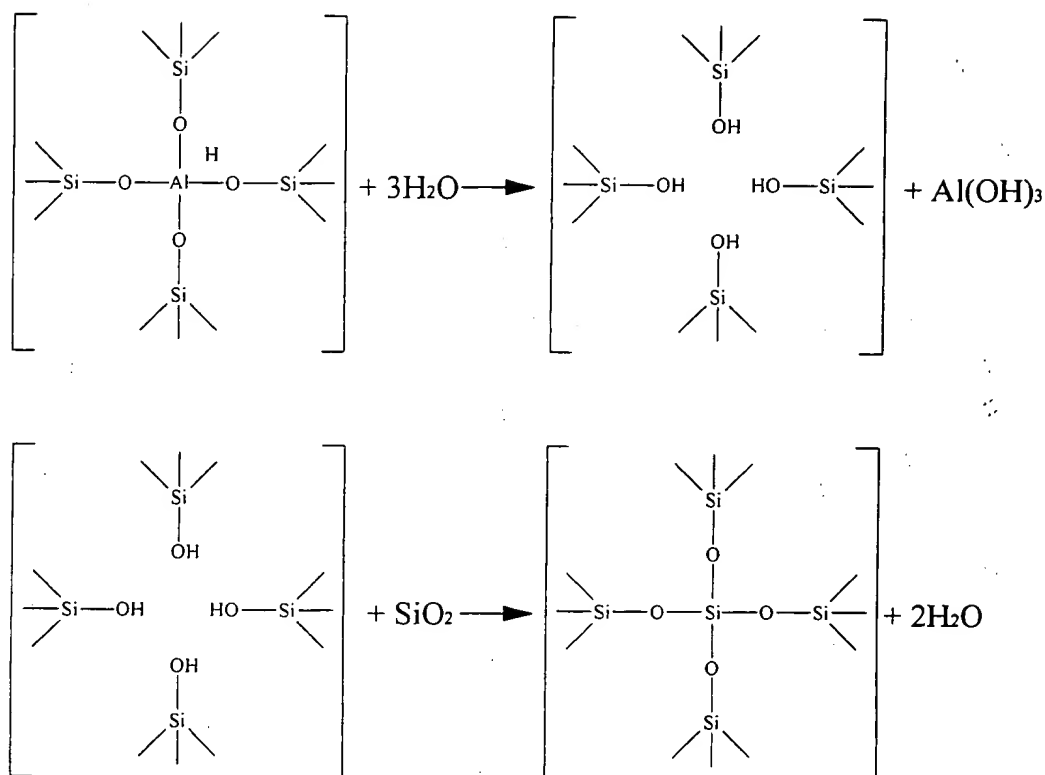


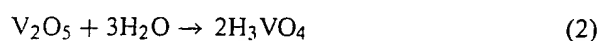
Fig. 13. $\delta = f(N)$ curves obtained from ^{129}Xe NMR spectra of the USY zeolites heated in 100% steam: (\blacktriangle) USY-R; (\blacksquare) V-USY; (\bullet) Na-USY; (\square) V-Na-USY.



Scheme 2. Mechanism for hydrolysis of framework Al and framework stabilization in USY zeolite by heat treatment in 100% steam [23–26].

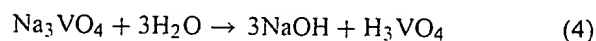
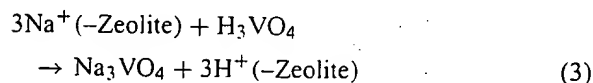
samples. Since the crystallinity values of USY-R and V-USY were not reduced so much compared with NaY, the number of the supercages in these samples were almost equal. Thus, the supercage structure of USY-R and V-USY was nearly maintained after the heat treatment in 100% steam. These results indicate that, when USY zeolite containing few sodium ions is heated in 100% steam, the supercage structure hardly changes and the deposited vanadium does not influence the framework destruction. In this respect, we believe that 'the framework stabilization mechanism' reported previously [23–26] and shown in Scheme 2 occurs generally. This mechanism means that first a hydrolysis between framework Al and H_2O in the atmosphere forms four Si-OH groups, a so-called 'hydroxyl nest', and then amorphous silicon gets into the hydroxyl nest. In this case, the deposited vanadium in USY zeolite changes into vanadic acid in the following reaction reported by Wormsbecher et al. [8] and Trujillo et al. [10] and functions as

an acid catalyst.



However, taking into account the fact that the unit-cell size and the crystallinity of V-USY were not much different from those of USY-R, the effect of the deposited vanadium on the acid catalysis was practically small because the amount of the deposited vanadium was only a few 0.2 wt.% in this study. Furthermore, the $\delta = f(N)$ curves of V-USY varied non-linearly at low N ($N < 1$), which represented the strong adsorption sites in the supercage. Before the heat treatment, however, the similar curvature appeared in V-USY, so the cationic EFAl such as AlOH^{2+} which corresponded to the strong adsorption sites were formed by only the calcination with the vanadium impregnation as discussed above. In other words, it is suggested that the curvature originated from those cationic species present before the heat treatment in 100% steam.

In the case of the samples containing a number of sodium ions, $\partial\delta/\partial N$ of V-Na-USY was three times larger than that of Na-USY. Thus, the supercage void volume of V-Na-USY was much smaller than that of Na-USY. This result indicates that the synergistic effect between the sodium ions and a few deposited vanadium on the framework destruction in 100% steam was tremendous. In this respect, Xu et al. suggested that a few vanadium ions promoted the formation of NaOH [12,13], so we propose that after reaction (2), two following reactions occur successively and as a result an increase in the NaOH content causes the framework destruction remarkably.



This proposal is based on the previous report that the solubility of quartz was directly proportional to the base concentration under hydrothermal conditions [14], and the dissolution of the zeolite crystal never stops when steam is supplied continually. In other words, the deposited vanadium functions as vanadic acid, catalyzes the above reactions which convert framework Na^+ into NaOH, and is not consumed by the reaction with the zeolite matrix elements claimed by the previous authors [11,27,28]. Consequently, we believe that the framework destruction occurs remarkably in the presence of a number of sodium ions and steam when only a few vanadium ions are deposited. This conclusion almost agrees with Pine [9] and Trujillo et al. [10], who claimed that the deposited vanadium functioned as a catalyst.

The crystallinity of V-Na-USY, however, was about only 1.7 times larger than that of Na-USY, which did

not much correspond to the $\partial\delta/\partial N$ analysis as mentioned above. This discrepancy can be solved by calculating the 'effective' void volume of the supercage (V_E) in these samples. Namely, based on the assumption that the reciprocal of the $\partial\delta/\partial N$, which represents the relative void volume of the supercage (V_R), in NaY is referred to 100%, V_R values in these samples are calculated. Furthermore, the value of V_R divided by the crystallinity, which generally corresponds to the number of the supercages, can be considered as V_E referred to 100% in NaY because in the case of a standard material such as NaY the supercage is not plugged at all and V_E is equal to 100%. This result is shown in Table 6. In USY-R, V-USY and Na-USY, V_E was more than 90%, so that the supercage was not much plugged, while only in V-Na-USY V_E was 58%, therefore, the supercage was plugged partially. Taking into account the fact that V_E was less than 60% in only the zeolite containing both a few vanadium ions and a number of sodium ions, one can conclude that the compounds formed between the vanadium and the sodium ion caused the supercage blockage. In this study, the atmosphere changed from 100% steam into the dry air immediately after the heat treatment, so that the H_2O content decreased rapidly and reaction (4) almost stopped. In this case, we believe that sodium vanadates such as Na_3VO_4 were left and as a result plugged the supercage. Additionally, δ 's of V-Na-USY was equal to that of Na-USY. It is clear that the blockage compounds in V-Na-USY had little influence on the xenon diffusion; therefore, they were present in the inside and not at the entrance of the supercage. In practical FCC processes, when catalysts or feed oils contain a few vanadium ions and alkaline compounds, it is possible that the vanadates formed cause a pore blockage and then a significant catalysis deactivation occurs.

Table 6

The void volume analysis of the supercage in the USY zeolites heated in 100% steam from $\delta = f(N)$ curve and crystallinity

Sample	The reciprocal of the slope of linear section of $\delta = f(N)$ curve (10^{20} atoms/ppm g)	The relative void volume of the supercage V_R obtained from $\delta = f(N)$ curve (%) ^a	The effective void volume of the supercage V_E (%) ^a
NaY	0.238	100	100
USY-R	0.217	91	98
V-USY	0.213	90	93
Na-USY	0.074	31	97
V-Na-USY	0.026	11	58

^a The values of NaY were taken as 100%.

4. Conclusions

In this study, the effect of the deposited vanadium on the dealumination and on the framework destruction of USY zeolite thermally in the presence of sodium ions and steam has been investigated by solid-state NMR. When USY zeolite containing few sodium ions was heated in a dry atmosphere, the formation of Si–OH groups, which corresponded to defect sites, and strong adsorption sites resulted from the dealumination. Thus, the former mainly caused an increase in the mean void volume per supercage and the latter originated from the formation of cationic EFAl in the supercages. In this case, the sodium ions inhibited the dealumination, and the effect of the deposited vanadium on the structural change was not large.

On the other hand, when USY zeolite containing few sodium ions was heated in 100% steam, the crystallinity and the supercage structure hardly changed although the dealumination occurred readily. This process did not depend on the deposited vanadium. Thus, we believe that the heat treatment in 100% steam causes a hydrolysis of framework Al and a framework stabilization due to inserting amorphous silicon atoms into 'hydroxyl nests' formed by four Si–OH groups. In the case of USY zeolite containing a number of sodium ions, the synergistic effect between a few deposited vanadium ions and the sodium ions on the framework destruction in 100% steam was tremendous, so we propose that the deposited vanadium functions as vanadic acid and catalyzes the conversion of the sodium ions into NaOH. Thus, an increase in the NaOH content promotes the 'dissolution' of the zeolite crystal, i.e. the framework destruction. In addition, in the case of the sample containing both a few vanadium ions and a number of sodium ions, the supercage was plugged partially after the heat treatment in 100% steam. We believe that the blockage compounds in the supercage are sodium vanadates.

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